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## Application Note SI-01037

### PL-DEAM, A Versatile Resin for Boronic Acids

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#### Introduction

PL-DEAM Resin is a versatile resin designed for use with boronic acids. Boronic acids are widely used in organic synthesis, particularly in Suzuki coupling reactions

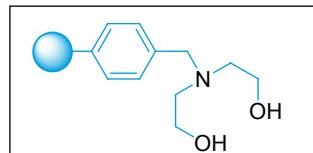


Figure 1. PL-DEAM Resin structure

- a key carbon-carbon bond forming reaction. PL-DEAM Resin is dual-purpose. It can be used as a scavenger resin to remove excess boronic acids from non-aqueous solutions [1], or to immobilize boronic acids for further functionalization [2,3]. A variety of commercially available boronic acids of the general formula R-B(OH)<sub>2</sub> can be attached to the resin, enabling modification of the side chain group R. This allows the creation of novel boronic acids to further increase the diversity in organic synthesis [4]. The products are readily cleaved from the resin using an aqueous acid/THF mixture. Alternatively, the Suzuki reaction can be carried out with the polymer bound boronic acid itself – ideal for producing biphenyl derivatives through reaction with iodobenzene compounds [5]. PL-DEAM MP-Resin can be used for boronic acid immobilization in polar protic solvents and is also a highly effective scavenger of metals from solution, in particular platinum and tin species.

#### Description

Polymer supported diethanolamine

#### Solvent compatibility - microporous

Toluene, DMF, THF, DCM, DCE, NMP, Dioxane

#### Solvent compatibility - macroporous

Toluene, DMF, THF, DCM, DCE, NMP, Dioxane, MeOH, EtOH, H<sub>2</sub>O

#### Applications

##### Scavenging of boronic acids from a Suzuki-Miyaura reaction

To a (5:1) ethanol: 2 M aq K<sub>2</sub>CO<sub>3</sub> solution, add aryl bromide or iodide (1.0 eq) and boronic acid (1.5 eq). Purge the reaction under a blanket of argon and add 10 mol percentage of a suitable palladium catalyst. At the end of the reaction the excess boronic acid can be effectively removed from the reaction mixture using PL-DEAM Resin, (2 eq) at room temperature for 2-12 hours. Some boronic acids may be scavenged more quickly than others. The HPLC run (A) shows a crude Suzuki reaction mixture with excess boronic acid and desired biaryl product. The HPLC run (B) shows that the boronic acid has been effectively scavenged.

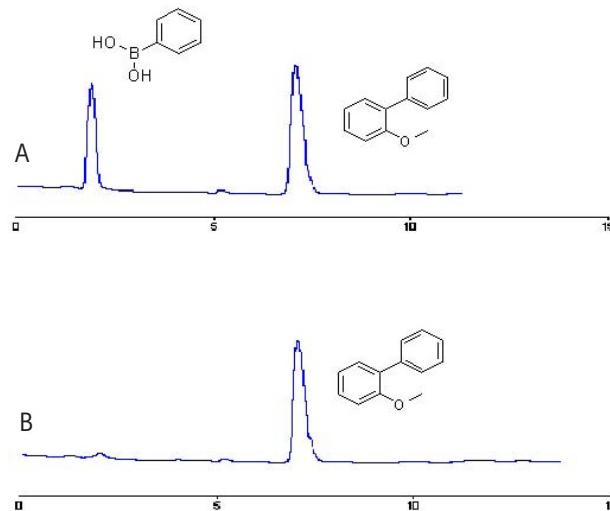


Figure 3. HPLC trace of a Suzuki-Miyaura reaction containing excess boronic acid (A) and post treatment with PL-DEAM Resin (B).

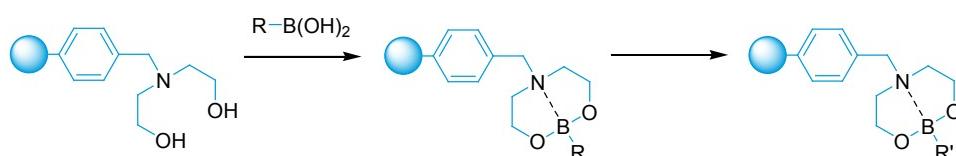


Figure 2. The modification and subsequent cleavage of an immobilized boronic acid using PL-DEAM Resin.

### **Immobilization of boronic acids to PL-DEAM Resin**

Dissolve the boronic acid (1.2 eq) in anhydrous tetrahydrofuran (THF). Then add PL-DEAM Resin (1 eq) and agitate for 1-3 hours. For larger scale applications, the solution should be cooled to 0 °C prior to the resin being added. After the reaction is complete, wash with anhydrous THF to remove any unchelated boronic acid. Subsequent reactions should be performed under anhydrous conditions.

### **Cleavage of boronic acids from PL-DEAM Resin**

The boronic acid can be easily cleaved from the resin using a solution of THF/water/acetic acid (90:5:5). The cleavage reaction should take 1-2 hours. After this time, remove the resin by filtration and wash the beads with more THF. The combined washings may then be evaporated to yield the desired boronic acid.

### **Metal scavenging applications of PL-DEAM MP-Resin**

PL-DEAM MP-Resin can be used for boronic acid immobilization in polar protic solvents and is also a highly effective scavenger of metals from solution, in particular platinum and tin species. Table 1 shows the residual metal concentration of various metals when a 1000 ppm solution of each metal has been scavenged by PL-DEAM MP-Resin. (Reactions were run in water).

Table 1. Residual metal concentration of various metals.

Metal	Residual Concentration (ppm)
Ruthenium	44.8
Lead	34.1
Palladium	10.4
Platinum	4.5
Tin	3.1

### **References**

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*These data represent typical results.*

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